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Stamped July 12, 1985

MEMORANDUM

SUBJECT: Interim Thresholds for Toxic Gas Generation Reactivity (§261.21(a)(5))

FROM: Eileen Claussen, Director
Characterization & Assessment Division (WH-562B)

TO: Solid Waste Branch Chiefs, Regions I to X

Over the past year, we have received many inquiries about how to evaluate wastes for reactivity (§261.21(a)(5)). We have initiated a number of studies in this area, and expect to propose a quantitative threshold for toxic gas generation reactivity in December of this year. On an interim basis, however, we feel strongly that wastes releasing more than the following levels of toxic gas should be regulated as hazardous wastes:

Total Available Cyanide:	250 mg HCN/Kg waste
Total Available Sulfide:	500 mg H_2S/Kg waste

The available cyanide or sulfide should be measured using the attached draft testing methods. Work currently being done on the agitation and waste introduction steps may result in significant changes in the subsequent proposed test. However, pending the conclusion of the investigations, we recommend use of this draft procedure.

I have attached a brief outline of the methodology we have employed to derive these interim thresholds. Work on estimating dispersion factors, however, is currently in progress. Any comments or suggestions you may have with respect to either the draft test method or the approach to establishing thresholds would be appreciated.

While you may wish to be flexible in your application of these levels and the attached test method, we believe the levels should apply in most cases. Should you have any specific questions, please call David Friedman of my staff at FTS 382-4770 (202-382-4770).

cc: Skinner
Lucero
Weddle
Corson
Friedman
Waste Management Division Directors, Regions I - X
Hotline

Attachment(s)

Attachment

Mismanagement scenario:

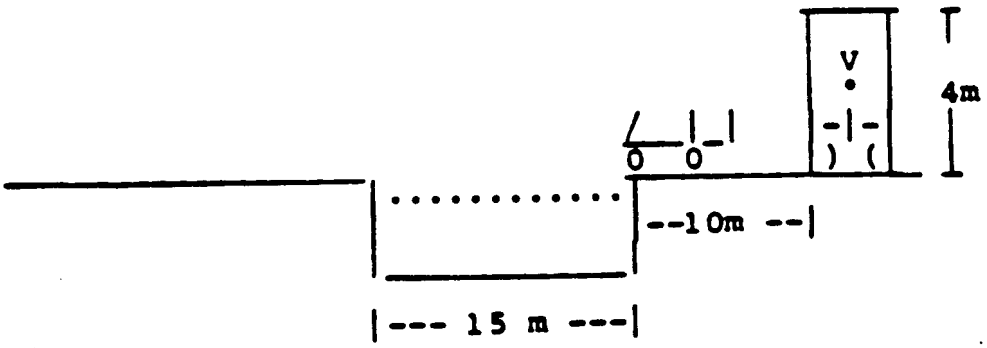
A truckload of waste is discharged into a pit containing acidic waste. As a result of the reaction of the waste with the acid, a rapid, high level release of toxic gas ensues. The objective of the characteristic is to identify those wastes which, if such an activity were to take place, pose a hazard to those persons in the general vicinity fo the disposal site.

Assume:

1. The truckload of waste contains 6130 kg of waste (about a 5 yd^3 dump truck @ 100 lbs/ft^3).
2. The velocity of the wind is 150 cm/sec (3.4 mph).
3. A person is standing 10 meters from the edge of the disposal pit.
4. Exposure to concentrations of:
   HCN above 10 mg/m^3 or
   H_2S above 20 mg/m^3
   pose an acute, immediate danger to human health.
5. The area of the pit over which the toxic gas is generated covers 225 m^2.
6. Before reaching an exposed individual the plume of contaminated air disperses, in a linear manner, to a height of 4 meters.

Then:

1. The minimum toxic gas release rate that would have to be present to exceed the danger level can be calculated using the following model.



2. Total available Toxicant level then that poses a hazard can be calculated as follows:

V is a hypothetical volume of air to which an individual is exposed. Since the pit is 15 meters wide, and V is assumed to be 1.5 m thick, V = 15 m wide x 4 m high x 1.5 m thick = 90 m^3

T is the time it takes for a given volume of air to travel across the surface of the pit and become contaminated with toxic gas. Since the wind speed is 150 cm/sec, and the volume slice is assumed to be 1.5 m thick, T = 10 seconds

C is concentration in mg/m^3 of toxicant that poses a danger.

A is the amount of toxicant contained in V when V is contaminated to a level that poses a health hazard. A = V x C. Since a given "slice" of air takes 10 seconds to move across the pit, this amount of toxicant can be generated over 10 seconds.

M is mass of waste dumped into the pit.

R is the total available toxicant necessary to pose a hazard as measured using the attached test protocol.

$$= \frac{\text{Amount of toxic gas that has to be released/length of test}}{\text{Mass of waste available to release } H_2S}$$

$$= \frac{(A)(1800/T)}{(M/\text{Percent of pit area available to contaminate air volume in any given unit of time})}$$

$$= \frac{(V)(C)(1800/T)}{(M/10)}$$

$$= \frac{(90)(C)(1800/10)}{(6130/10)}$$

$$= \frac{(90)(C)(180)}{(613)}$$

$$= 26.4\ (C)$$

= 264 mg/Kg total available cyanide

= 528 mg/Kg total available sulfide

3. As an added margin of safety, we accordingly recommend the action levels of:

Total Available Cyanide: 250 mg HCN/Kg waste
Total Available Sulfide: 500 mg H_2S/Kg waste

TEST METHOD TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES

1. Scope and Application

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2. Summary of Method

2.1 An aliquot of acid is acidified to pH 2 in a closed system. The gas generated is swept into a scrubber. The analyte is quantified. The procedure for quantifying the cyanide is Method 9010 starting with Step 7.3.5. of that method (attached)

3. Sample Handling and Preservation

3.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

3.2 It is suggested that samples of cyanide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Storage of samples should be under refrigeration and in the dark.

3.3 Testing should be performed in a ventilated hood.

4. Apparatus (see Figure 1)

4.1 Three-neck, round-bottom flask with 24/40 ground-glass joints, 500 ml.

4.2 Stirring apparatus to achieve approximately 30 rpm. This may be a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

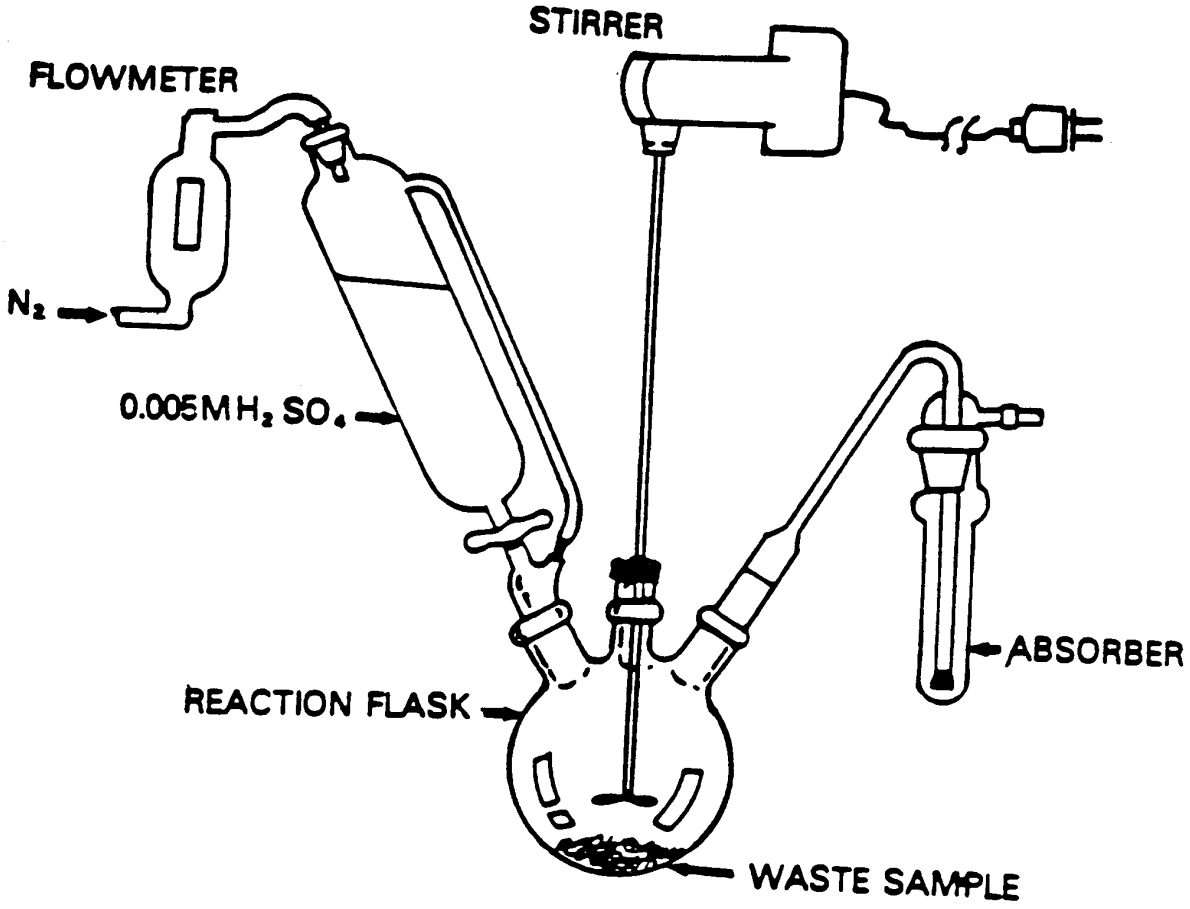
4.3 Separatory funnel with pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.4 Flexible tubing for connection from nitrogen supply to apparatus.

4.5 Water-pumped or oil-pumped nitrogen gas with two-stage regulator.

4.6 Rotometer for monitoring nitrogen gas flow rate.

Figure 1


STIRRER
FLOWMETER
N_2
0.005M H_2SO_4
ABSORBER
REACTION FLASK
WASTE SAMPLE

5.0 Reagents

5.1 Sulfuric acid 0.005 M

5.2 Cyanide reference solution: Dissolve approximately 2.5 gm of KOH and 2.51 gm of KCN in 1 liter of distilled water. Cyanide concentration in this solution is 1 mg/ml.

5.3 NaOH solution, 1.25N: dissolve 50 gm of NaOH in distilled water and dilute to 1 liter with distilled water.

5.4 NaOH solution, 0.25N: Dilute 200 mL of sodium hydroxide solution to 1 liter with distilled water.

5.5 Stock cyanide solution, 1 mg/ml: Dissolve 2.51 gm KCN and 2 gm KOH in 1 liter of distilled water. Standardized with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml - 1 mg CN.

5.6 Intermediate cyanide solution: Dilute 50 ml of stock solution to 1 liter with distilled water.

5.7 Standard cyanide solution, 5 mg/L: Prepare fresh daily by diluting 100. ml of intermediate solution to 1 liter with distilled water and store in a glass-stoppered bottle.

5.8 Silver nitrate solution: Prepare by crushing approximately 5 gm of $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh 3.3 gm dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter.

5.9 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 ml of acetone.

5.10 Methyl red indicator: Prepare 0.02 gm dissolved in 60 ml distilled water and 40 ml acetic acid.

6 System Check

6.1 The operation of the system can be checked using the cyanide reference solution. The reference solution can be used to verify system operation.

7.0 Procedure

7.1 Add 500 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with distilled water to obtain an adequate depth of liquid.

7.2 Close the system and adjust the flow rate of nitrogen using the rotometer. Flow should be 60 ml/min.

7.3 Add 10 gm of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough acid to fill the system 1/2 full. While starting the 30 minute test period.

7.5 Begin stirring while the acid is entering the round bottomed flask.

7.6 After 30 minutes close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by Method 9010, starting with step 7.3.5. of the method (attached).

8.0 Calculations

8.1 Determine the specific rate of release of HCN

-Concentration of HCN in diluted scrubber solution (mg/L) = A
This is obtained from Method 9010.

-Volume of solution in scrubber (l) = L

-Weight of waste used (Kg) = W

-Time of measurement = Time N2 stopped - Time N2 started (seconds) = S

$$R = \text{specific rate of release} = \frac{A \cdot L}{W \cdot S}$$

Total available HCN = R • 1800 mg/Kg

METHOD 9010

TOTAL AND AMENABLE CYANIDE

1.0 Scope and Application

1.1 Method 9010 is used to determine the concentration of inorganic cyanide in a waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9010 does not determine the "reactive" cyanide content of wastes containing iron-cyanide complexes. (As an alternative to Method 9010, autoanalyzers may be used for cyanide analysis if the analyst adheres to the precautions and quality control requirements specified in this method.)

2.0 Summary of Method

2.1 The waste is divided into two parts. One is chlorinated to destroy susceptible complexes. Each part is then distilled to remove interferences and analyzed for cyanide. The fraction amenable to chlorination is determined by the difference in values.

2.2. During the distillation, cyanide is converted to hydrogen cyanide vapor, which is trapped in a scrubber containing sodium hydroxide solution. This solution is then titrated with standard silver nitrate.

3.0 Interferences

3.1 Sulfides interfere with the titration. They may be precipitated with cadmium

3.2 Fatty acids form soaps under alkaline titration conditions and interfere. They may be extracted with a suitable solvent.

3.3 Oxidizing agents may decompose the cyanide. They may be treated with ascorbic acid.

3.4 Thiocyanate presence will interfere by distilling over in the procedure. This can be prevented by adding magnesium chloride.

3.5 Aldehydes and ketones may convert cyanide to cyanohydrin under the acid distillation conditions.

4.0 Apparatus and Materials

4.1 Microburet, 5.0 ml, for titration.

4.1 Flasks, condenser, and tubing are needed as shown in Figure 1. The boiling flash should be of 1-liter size with inlet tube and provision for a condenser. The gas absorber may be a Fisher-Milligan scrubber. Assemble as shown in Figure 1.

Figure 1

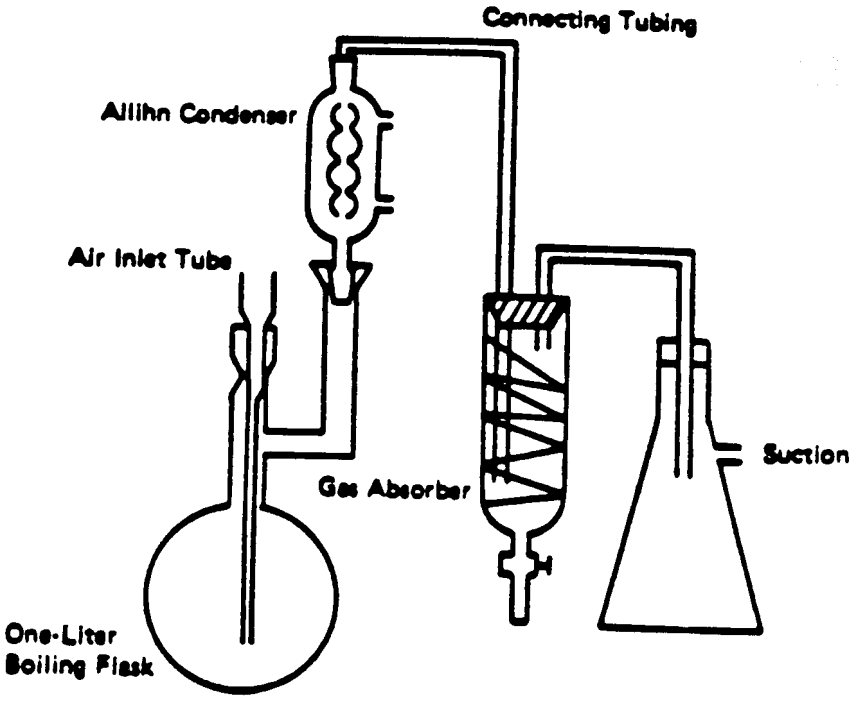


Figure 1. Apparatus for cyanide distillation.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193) or better quality: Water should be monitored for impurities.

5.2 Calcium hypochlorite solution: Dissolve 5 g of hypochlorite, Ca(OCl2), in 100 ml of Type II water.

5.3 Sodium hydroxide solution (1.25 N): Dissolve 50 g of sodium hydroxide (NaOH) in Type II water and dilute to 1 liter.

5.4 Ascorbic acid: cyrstals.

5.5 Potassium iodide-starch paper.

5.6 Lead acetate paper.

5.7 Cadmium carbonate (powdered).

5.8 Hexane.

5.9 Acetic acid solution (1:9).

5.10 Conc. H_2SO_4

5.11 Silver nitrate standard solution (0.0192 N): Dry 5 g $AgNO_3$ crystals to constant weight at 40° C. Weigh out 3.2647 g and dissolve in Type II water. Dilute 1000 ml (1 ml = 1 mg CN).

5.12 Rhodanine indicator solution: Dissolve 20 mg p-dimethyl-amino-benzalrhodanine in 100 ml acetone.

5.13 Magnesium chloride solution: Weigh 510 g of $MgCl_2C6H_2O$ into a 1-liter volumetric flask. Dissolve and bring to volume with Type II water.

6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples should be collected in plastic or glass containers of 1-liter size or larger. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of water.

6.4 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH is greater than or equal to 12) at the time of collection.

6.5 Samples should be refrigerated to 4°C when possible and analyzed as soon as possible.

7.0 Procedure

7.1 If interferences are known or suspected to be present, test and treat the sample as follows.

7.1.1 Sulfides: If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the sample, than the amount required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates of the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to use for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide.

7.1.2 Fatty acids: Acidify the sample with acetic acid (1:9) to pH 6.0 to 7.0. CAUTION: Toxic hydrogen cyanide can be generated in an acid solution. This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed. Then extract with isooctane, hexane, or chloroform (preference in order listed) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

7.1.3 Oxidizing agents: Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper). A blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

7.2 Chlorination of a sample aliquot

7.2.1 Take a 500-mL sample aliquot or a sample volume diluted to 500 ml. Add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide solution (1.25 N). CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1-liter beaker by a magnetic stirring device.

7.2.2 Test for residual chlorine with KI-starch paper and maintain this excess for 1 hr, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

7.2.3 After 1 hr, add 0.5-g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

7.3 Take the aliquot treated in Section 7.2 plus either a second 500-ml aliquot of the untreated sample or an untreated aliquot diluted to 500 ml in the 1-liter boiling flask and separately distill as follows.

7.3.1 Add 50 mL of sodium hydroxide (1.25 N) to the absorbing tube and dilute if necessary with Type II water to obtain an adequate

depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

7.3.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube. CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. The air rate must therefore occasionally be adjusted to prevent the solution in the foiling flask from backing up into the air inlet tube.

7.3.3 Slowly add 25 ml conc. sulfuric acid through the air inlet tube. Rinse the tube with Type II water and allow the air flow to mix the flask contents for 3 min. Pour 20 ml of magnesium chloride solution into the air inlet and wash down with a stream of water.

7.3.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for 1 hr. Turn off the heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

7.3.5 Drain the solution from the absorber into a 250-mL volumetric flask and bring to volume with Type II water washings from the absorber tube.

7.4 Titration

7.4.1 Add the solution or an aliquot diluted to 250 ml to a 500-ml erlenmeyer flask. Add 10-12 drops rhodanine indicator.

7.4.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a Type II water blank using the same amount of sodium hydroxide and indicator as in the sample.

7.4.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-ml microburet may be conveniently used to obtain precise titration.

7.5 Titrate a blank using Type II water in an identical manner.

7.6 Calculation:

1. CN, mg/L =
{[(A - B) 1,000] ÷ (ml orig. sample)} X [250 ÷ ml of aliquot titrated]

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

2. Cyanide amenable to chlorination:

CN, mg/l = C - D

where:

C = mg/l total cyanide in unchlorinated aliquot
D = mg/l total cyanide in chlorinated aliquot

7.7 Duplicates, spiked standards, and check standards should be routinely analyzed.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

TEST METHOD TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES

1. SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that waste which are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the evolved hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2. SUMMARY OF METHOD

2.1 An aliquot of acid is acidified to pH 2 in a closed system. The gas generated is swept into a scrubber. The analyte is quantified. The procedure for quantifying the sulfide is given in Method 376.1.

3. SAMPLE HANDLING AND PRESERVATION

3.1 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and addition of zinc acetate to the sample, this will cause dilution of the sample, increase the ionic strength and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

4. APPARATUS (See Figure 1)

4.1 Three-neck, round-bottom flask, with 24/40 ground-glass joints, 500-ml.

4.2 Stirring apparatus to achieve approximate 30 rpm. This may be a rotating magnet and stirring bar combination or an overhead motor-driven propellor stirrer.

4.3 Separatory funnel with pressure equalizing tube and 24/40 ground glass joint and teflon sleeve.

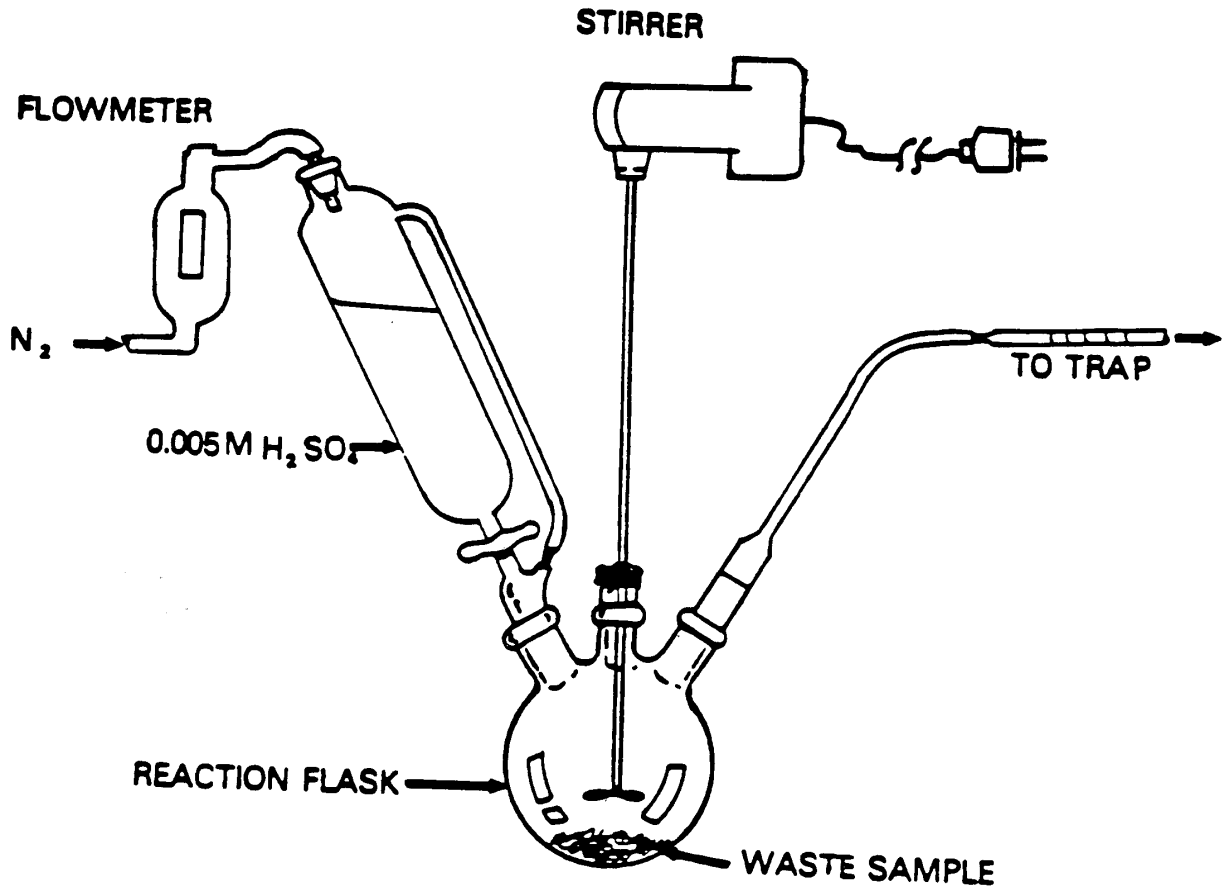
4.4 Flexible tubing for connection from nitrogen supply to apparatus.

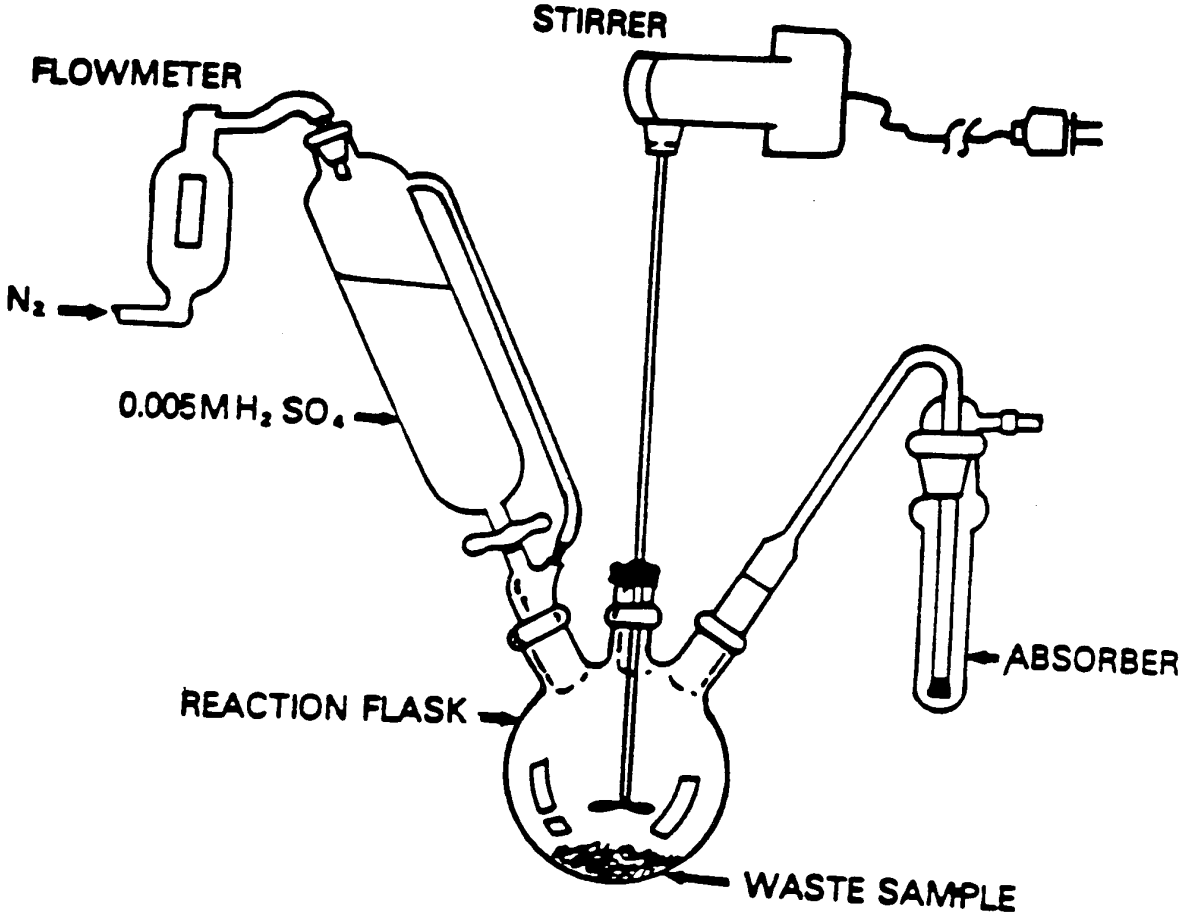
4.5 Water pumped or oil pumped nitrogen gas with two stage regulator.

4.6 Rotometer for monitoring nitrogen gas flow rate.

4.7 Industrial hygiene type detector tube for sulfide (100-2000 ppm range).

Figure 1


STIRRER
FLOWMETER
N_2
TO TRAP
0.005 M H_2SO_4
REACTION FLASK
WASTE SAMPLE


STIRRER
FLOWMETER
N_2
0.005M H_2SO_4
REACTION FLASK
ABSORBER
WASTE SAMPLE

5. REAGENTS

5.1 Sulfuric acid, 0.005 M

5.2 Sulfide reference solution: Dissolve 4.02 g of $Na_2S \cdot 9H_2O$ in 1.0 liters distilled water. This is 680 ppm hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100 ppm to 680 ppm).

5.5 NaOH solution, 1.25N: dissolve 50 gm of NaOH in distilled water and dilute to 1 liter with distilled water.

5.6 NaOH solution, 0.25N: Dilute 200 ml of sodium hydroxide solution to 1 liter with distilled water.

6. SYSTEM CHECK

6.1 The operation of the system can be checked using the sulfide reference solution. The reference solution can be used to verify system operation.

7. PROCEDURE

The procedure is dependent on the method chosen for quantification.

-If an absorbent tube indicator is used for quantification, the analyst should start the procedure with Step 7.2.0

-If another procedure is chosen, the analyst should start the procedure with 7.1.0

<u>7.1.0 Procedure employing scrubber solution with wet method quantification</u>

7.1.1 Add 500 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with distilled water to obtain an adequate depth of liquid.

7.1.2 Assemble the system and adjust the flow rate of nitrogen using the rotometer. Flow should be 60 mL/min.

7.1.3 Add 10 gm of the waste to be tested to the system.

7.1.4 With the nitrogen flowing, add enough acid to fill the flask 1/2 full, while starting the 30 minute test period.

7.1.5 Begin stirring while the acid is entering the round bottomed flask.

7.1.6 After 30 minutes close off the nitrogen and disconnect the scrubber. Determine the amount of sulfide in the scrubber by Method 376.1 (enclosed). following methods

7.1.7 Go to Section 8.1 for calculation of specific rate of release.

<u>7.2.0 Procedure employing dry absorbent indicator tube for quantification.</u>

7.2.1 Assemble the system with the absorber tube in place, making sure that the tube has the proper orientation (see manufacturer's literature).

7.2.2 Adjust the flow rate of nitrogen to be 60 ml/min using the rotometer.

7.2.3 Add 10 gm of waste to the system.

7.2.4 Start the test by adding enough acid of pH 2 to fill the round bottom flask half full.

7.2.5 After 30 minutes, read the length of the stain on the indicator tube. Follow the manufacturer's directions in determining the concentration of sulfide in the gas using the length of the stain and the amount of gas passed through the tube.

7.2.6 Go to Section 8.2 to calculate the specific rate of release.

8. CALCULATIONS

8.1 Determine the specific rate of release of H2S

Concentration of H_2S in scrubber (mg/L). This is obtained from method 376.1 or 376.2. = A

Volume of solution in scrubber (l) = L

Weight of waste used (kg) = W

Time of experiment = Time N_2 stopped - Time N_2 started (seconds) = S

R = spec. rate of release = $(A \cdot L) \div (W \cdot S)$

Total available H_2S (mg/kg) = R x 1800 mg/kg

8.2 Calculation for absorber tube determination of sulfide

Final detector tube reading (ul) = L

Flow rate N_2 through tube (ml/min) = V

Time of flow (min) = T

Conversion factor = 1.1 <Note: this is meant to be 1.42 based on below> = D

Weight of sample (kg) = W

Specific rate of release = R

$R = [L \div (1000 \cdot W)] \cdot (1.42)$ = mg/kg of H_2S

SULFIDE

Method 376.1 (Titrimetric, Iodine)

STORET NO. Total 00745
Dissolved 00746

1. Scope and application

1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

1.3 This method is suitable for the measurement of sulfide in concentration above 1 mg/l.

2. Summary of method

2.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with sodium thiosulfate or phenylarsine oxide.

3. Comments

3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.

3.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

3.3 If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.

4. Apparatus: Ordinary laboratory glassware.

5. Reagents

5.1 Hydrochloric acid, HCl, 6 N

5.2 Standard iodine solution, 0.0250 N: Dissolve 20 to 25 g KI in a little water in a liter volumetric and add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.0250 N sodium thiosulfate or phenylarsine oxide using a starch indicator.

5.3 Phenylarsine oxide 0.0250 N: commercially available.

5.4 Starch indicator: commercially available.

5.5 Procedure for standardization (see Residual Chlorine-iodometric titration Method 330.3, section 5.15).

Approved for NPDES
Issued 1971
Editorial revision 1978

6. Procedure

6.1 Unprecipitated sample

6.1.1 Place a known amount of standard iodine solution (5.2) into a 500 ml flask. The amount should be estimated to be in excess of the amount of sulfide expected.

6.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.

6.1.3 Add 2 ml of 6 N HCl (5.1).

6.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.

6.1.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used in performing steps 6.1.1 and 6.1.5.

6.1.6. Titrate with the reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution (5.3)) using a starch indicator (5.4) until the blue color disappears. Record the number of milliliters used.

6.2 Precipitated samples

6.2.1 Add the reagents to the sample in the original bottle. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3 Dewatered samples

6.3.1 Return the glass fibre filter paper which contains the sample to the original bottle. Add 200 ml distilled water. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3.2 The calculations (7) should be based on the volume of original sample put through the filter.

7. Calculations

7.1 One ml of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.

7.2 Use the formula

$$\text{mg/l sulfide} = [400\ (A - B)] \div \text{ml sample}$$

where:

A = ml of 0.0250 N standard iodine solution (5.2)
B = ml of 0.0250N standard reducing sodium thosulfate or phenylarsine oxide) solution (5.3).

8. Precision and accuracy

8.1 Precision and accuracy for this method have not been determined.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 505, Method 428D, (1975).